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HOT WATER PROCESSING OF ATHABASCA OIL SANDS: III. LABORATORY STUDIES ON SETTLING, MIDDLINGS VISCOSITY, AND INFLUENCE OF ELECTROLYTES

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INTRODUCTION

The Athabasca sands yield up their oil in the hot water extraction process by floating as a froth while the sand sinks in a separation vessel. The medium in which this settling occurs is a suspension of the mineral fines in hot water called middlings. The settling may seem to involve only a simple exercise in Stokes law to predict and optimize the results. However, when detailed consideration is given to continuous large scale operations, a number of complicating factors arise. For example, economic and engineering factors dictate that the middlings be recycled through the process (1). The plant feed contains varying amounts of fine material, and their removal is accomplished through a drag stream from the middlings recycle. The magnitude of the drag stream is determined by the fines content of the plant feed and the density of the middlings. Economic and engineering factors again dictate this density be as high as settling operability will allow. The laboratory study of this critical factor directed us to some experimental parameters of primary importance in the hot water extraction process.

Conditioning Procedure Used in Settling Experiments

The second paper of this series describes a laboratory conditioning procedure whose characteristics are almost all closely comparable to the large scale apparatus of the pilot plant (2). The one remaining point of concern was the mineral content of the froth -- laboratory froth in general had a higher content of mineral. A specific procedure was discovered with the stirred reactor which solved this problem. The resolution of this last point of difference is important for the work to be presented because it gave us complete confidence that we could proceed with a laboratory study of settling; the results would be meaningful for large scale work.

EXPERIMENTAL

Conditioning is generally regarded as a process carried out at a chosen "solids content", e.g., 80 percent solids means oil + mineral is 80 percent with 20 percent water. The essence of the method used in this paper is described in Table 1 as "New Procedure". Water was added in increments at the stated intervals during the conditioning in the stirred reactor. The remainder of the procedure up to the settling process is as follows. Flooding water was added, the stirrer slowly speeded up to 300 r.p.m. and then slowly stopped. Variations in procedure such as with the rich oil sand are made when the viscosity of the mixture requires it. All operations and measurements are at 85°C.

RESULTS

The results of the stepwise addition of water in conditioning are shown in Table 1. The first results from the "New Procedure" were most gratifying in that not only was mineral low but the results were uniform. Earlier laboratory froth samples characteristically have a relatively large random variance. The experiments listed under the variations were to test the unique requirements of each stage. All the details proved to be necessary. Experiments were also performed which showed that the rate of heating or preheating had no influence on the result. In the stage at low water content, stirring produces high shear in the mixture. We believe this action is responsible for reducing the content of fine mineral in the oil globules. The action of the other essential parts of the procedure is understood in terms of the shear and the particle size characteristics of the mineral in the froth.

Laboratory Recycle of Middlings: High-fines Oil Sand with Middlings of Normal Viscosity

In the basic laboratory operation of settling for a given batch of oil sand, the layer of froth is skimmed off, the middlings decanted after a chosen interval of settling, and the sand tailings remain in the vessel. Middlings from one run can, as chosen, be used in conditioning and flooding in the processing of the next batch of oil sand feed. In successive cycles of this process with a properly chosen "drag stream", middlings density can be built up and will proceed to inoperability. Many aspects of hot water processing, including quantitative, are formally related to multi-stage solvent extraction; laboratory batch procedure is related in this way to the continuous pilot plant. With a laboratory batch procedure, independent parameters can be set and measurements made of as many dependent variables as possible to characterize the system. We wished to examine all possible effects that might be operating in the settling, so that as wide as possible a range of characterizing variables were obtained.

EXPERIMENTAL

The "New Procedure" of Table 1 was used for the conditioning and flooding was done by adding the proper amount of water and/or recycle middlings. This stirring-for-flooding procedure is especially useful because a series of density measurements over any period of time can be made with pipetted samples, the mixture re-stirred, allowed to settle the desired time, and then decanted. The following sample sequence was used:

1. "Immediate density" - taken as soon as possible after stirring is stopped.
2. Similar sample after 2 min. settling.
3. Similar sample after 5 minutes.
4. Similar sample after 15 minutes.
5. Decanted middlings were stirred and a uniform sample taken.

The density sample was taken in a specially designed weight pipette with a large opening. The two-minute density sample was analyzed for oil and mineral.

Viscosity measurements on a suspension of mineral and oil are difficult, particularly when special rheological measurements are to be made, e.g., to detect small thixotropic effects. Early measurements in the pilot plant laboratory were made by settling the middlings for 9-15 minutes and making the measurements on the supernatent liquid. We found the procedure satisfactory and thereafter used it so that our results could be compared directly to the data from the continuous process.

Conductivity measurements are also difficult, primarily because the oil in the middlings fouls the electrodes. Two short heavy platinum wires in a fixed support proved to be rugged for cleaning and of adequate sensitivity. Analysis for oil and mineral were performed on the froth and tailings so that overall balances could be reported. Also, the primary froth yield would be used as our basic indicator to show whether in a given batch the settling was operable or inoperable. A number of intervals of settling prior to decantation were used: 0.58, 2, and 15 minutes. As will be noted in the results, the differences in behavior all were as might be expected; consequently, most of the work was done at one interval, 2 min.

RESULTS

The different facets of the experimental results resolve themselves in several major groups that are presented below.

Froth and Middlings - analytical results and other measurements:

These results from several characteristic runs are shown in Tables 2 and 3. Table 2 represents a sequence which was inoperable at the ninth cycle. The series shown in Table 3 was terminated when all signs indicated an incipient inoperability. The final middlings were then available for further detailed studies. The following points may be noted:

a. The effect of recycling middlings in increasing primary froth yield is one of the last links establishing laboratory processing as being comparable to pilot plant in yield. Evidence shows that the increase comes from the additional opportunity for oil in middlings to float as it is recycled. An alternative explanation lies in increased buoyancy from middlings of higher density. Experiments are in progress to establish which one or if both factors are important.

TABLE 1

TESTING OF CONDITIONING WITH STEPWISE
DECREASE IN SOLIDS CONTENT: EFFECT ON MINERAL CONTENT OF FROTH

Conditions: 200 g. Pit A Lot 25 oil sand (10% oil)
3-inch stirred reactor, 50 r.p.m.; conditioning temperature 85°C; 200 ml. flooding water at 85°C

Procedure of Conditioning[(1)]	% Recovered Bitumen in Froth	Midd.	Tails	% Mineral in Froth, D.B.
Former standard procedure:				
80% solids, 10 min.	54.2	27.0	18.8	-8.3
	54.3	15.7	30.0	6.7
New Procedure:				
85% 5 min ⟶ 80% 3 min ⟶ 75% 3 min ⟶ 70% 3 min	58.5	25.2	16.3	4.5
	63.2	22.7	14.1	4.6
	60.0	27.5	12.5	4.7
90% 5 min ⟶ 80% 3 min ⟶ 70% 3 min	62.6	23.0	14.4	0[(2)]
	70.3	19.0	11.7	4.2
Variations for Test Purposes				
85% 5 min	63.3	23.8	12.9	8.2
	64.3	20.6	15.1	7.9
70% solids 12 min	39.7	39.4	20.7	10.0
	46.6	36.2	17.2	8.5
85% 5 min ⟶ 70% 3 min	64.1	24.0	11.9	6.5
Confirmation with different type oil sand: Rich oil sand, 13.5% oil, with 20% seam clay added				
Former procedure:				
80% 10 min	63.9	23.6	12.5	5.8
New Procedure: 85% 5 min ⟶ 80% 3 min ⟶ 75% 3 min ⟶ 70% 3 min ⟶ 65% 3 min	80.2	13.0	6.8	3.0

(1) % solids in conditioning refers to oil + mineral; i.e., 80% solids in 20% water.

(2) This result may be in part analytical error, but it shows a low level of mineral.

TABLE 2

BATCH RECYCLE RUNS ON PIT A LOT 25 OIL SAND:
ANALYTICAL RESULTS AND RELATED DATA

Conditions: Oil sand, 10% oil; 3" stirred reactor
50 RPM, 15 minute middlings decant,
0.6 #/ton NaOH

Cycle No.	Midd pH	Primary* Froth Yield	% of Recovered Bitumen in:* Froth	Midd	Tails	% Min. in Froth: Min.(D.B.)	Analysis of Midd % Min	% Oil
1	8.3	38.5	43.8	40.2	16.0	10.1**	7.3	3.0
2	8.3	56.2	46.1	39.5	14.4	8.3	9.1	4.1
3	8.0	56.2	43.8	44.3	11.9	10.7	10.7	4.8
4	8.2	54.8	38.2	49.7	12.1	14.0	13.6	5.6
5	8.2	56.6	39.9	46.6	13.5	14.9	14.3	5.6
6	8.4	60.1	42.0	42.8	15.2	15.1	14.9	5.2
7	8.1	62.3	39.2	51.3	9.5	13.2	15.0	5.9
8	8.2	56.2	34.8	54.3	10.9	19.0	15.0	6.3
9†	7.8	9.5	6.7	93.3	-	62.0	42.3	5.8

*Primary froth yield is calculated on the basis of one batch input. The bitumen distribution includes oil recycled in middlings as well.

**This value is unexpectedly high and may well be in error.

† Conditioning with middlings in place of fresh water.

TABLE 3

BATCH RECYCLE RUNS ON A SILTY OIL SAND: ANALYTICAL RESULTS AND RELATED DATA

Conditions: 200 g. September Shaley Pit A, 9% oil; 3" stirred reactor, 50 RPM; 2-minute middlings decant

Cycle No.	Caustic Loading #/Ton	Midd pH	% Primary Froth Yield	% of Recovered Bitumen in: Froth	Midd	Tails	% Min. in Froth D.B.	Analysis of Middlings % Min	% Oil	Conductance of Decanted Middlings
1	0.6	8.4	47.4	58.7	28.2	13.1	9.0	8.05	1.88	800
2	0.675	8.3	62.3	59.1	31.0	9.9	10.7	11.8	2.6	445
3	0.75	8.3	65.4	52.8	37.7	9.5	12.0	14.1	3.6	1390
4	0.75	8.5	68.5	53.4	37.2	9.4	13.2	17.6	3.6	1780
5	0.675	8.3	77.8	51.9	40.9	7.2	14.4	17.9	4.5	1890
6	0.75	8.3	62.7	49.8	42.3	7.9	13.9	19.0	4.3	2300
7	0.875	8.35	61.5	44.4	49.9	5.7	16.9	20.4	4.0	2275

b. Mineral in the froth - an important measure of the quality of the froth - is closely related to middlings density. Since conditioning was with few exceptions done with fresh water, a large portion of the mineral in the froth was incorporated in the flooding through mechanical occlusion of water.
c. The "Recovered Bitumen" results demonstrate that as inoperability is reached, the oil becomes suspended more and more in the middlings.
d. Experiments interspersed in a series in which conditioning was done with middlings rather than fresh water demonstrated that high mineral in the froth and low primary froth yield result.

Settling as measured by successive density samples:

The time sequence of density samples taken 1 inch below the surface of the settling mixture can be analyzed to indicate any normal or abnormal settling behavior. The results are shown in Table 4.

Measurements of the rate of settling of mineral particles of different known sizes would provide a clear unambiguous answer as to rheological environment that obtains in the settling process. The results in Table 4 are only part of the data required for this absolute measurement. They do, however, give a strong indication that no abnormal viscosity is present even in the last runs which preceded inoperability.

For a number of samples, particle size data are available for the final middlings. In the customary analysis, cuts are made at 43 and 2 microns. These samples are not directly from the sequences in Table 4, but are from a sample of essentially the same properties.

Cycle	Settling Time for Decantations	Sand $>43\mu$	Silt Fraction $>2, <43\mu$	Clay Fraction $<2\mu$
1	2 min.	0.5	42	57
9	2 min.	0.5	43	56
9	0.58 min.	4.5	52	43
2	2 min.	2.5	47	50
9	2 min.	.5	54	45

If these results are interpreted with the density differences in Table 4, then the complete Stokes law comparisons of viscosities in the early and late cycles is made. There is no evidence for a thixotropic effect in these samples. The samples vary from 6 to 20 percent fine mineral.

Mineralogical analyses by X-ray diffraction have been made on these and a number of other samples in which the mineral was fractionate by sedimentation. Aside from the expected increase in the relative amount of clay in the smaller fractions, no fractionation of any mineral species has been observed.

Measurements with the Brookfield viscometer:

Conventional measurements of viscosity were made on samples of settled middlings in a further effort to detect thixotropic and other non-Newtonian rheology. With the Brookfiled viscometer measurements for the conventional shear stress-shear rate curve can be made. No evidence could be adduced for the existence of a yield stress in these samples. The procedure was designed to measure immediate viscosity and then the viscosity which developed as the instrument was in motion. This rheopectic viscosity is related to thixotropy, but the relative time rates of development are too complex to make any direct comparison of value.

Viscosity measurements for the experiments listed in Table 3 are shown in Figure 1. Plotting viscosity against density (or percent mineral) for different oil sands is one indication we have as to how one oil sand sample may differ from another in this aspect -- how high a density may be operable. In the heading of this main section, the term "normal" viscosity is used in the sense that this September Shaley Pit A gives a relatively low visoosity for a given density. We will see in the next section some results which we have called "abnormal" viscosity. These are relative terms, and as usual, normal and abnormal are defined in terms of common experience.

Conductimetric measurements:

In recycle experiments the caustic reagent dosage will accumulate and as expected the conductance slowly increases and levels off (because of the drag stream extraction effect). The results with these samples again are noted as "normal" behavior. Occasional unexpectedly low values of conductance are of no concern because they result from electrode fouling.

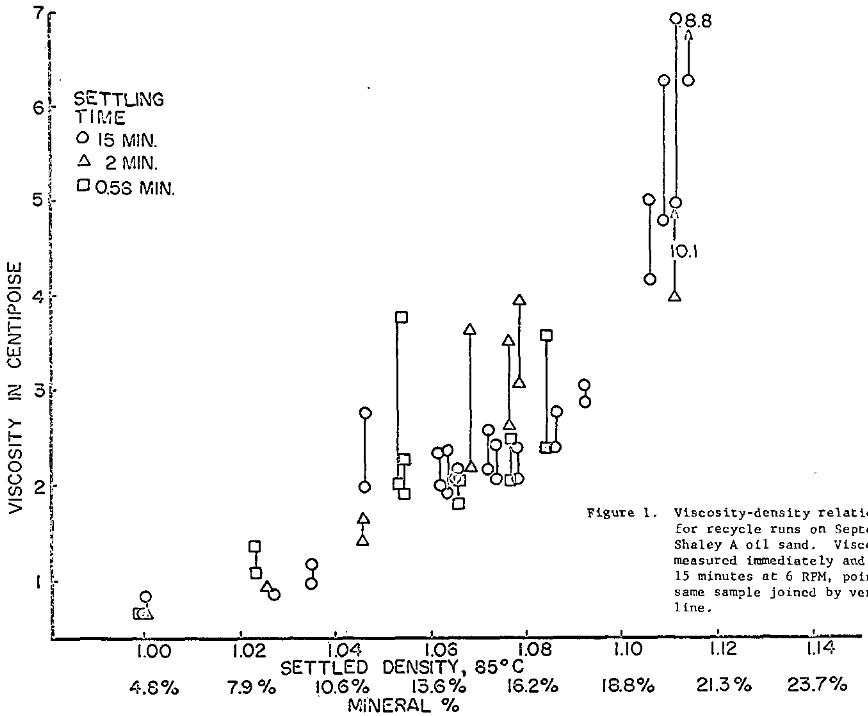

Figure 1. Viscosity-density relationships for recycle runs on September Shaley A oil sand. Viscosity measured immediately and after 15 minutes at 6 RPM, points for same sample joined by vertical line.

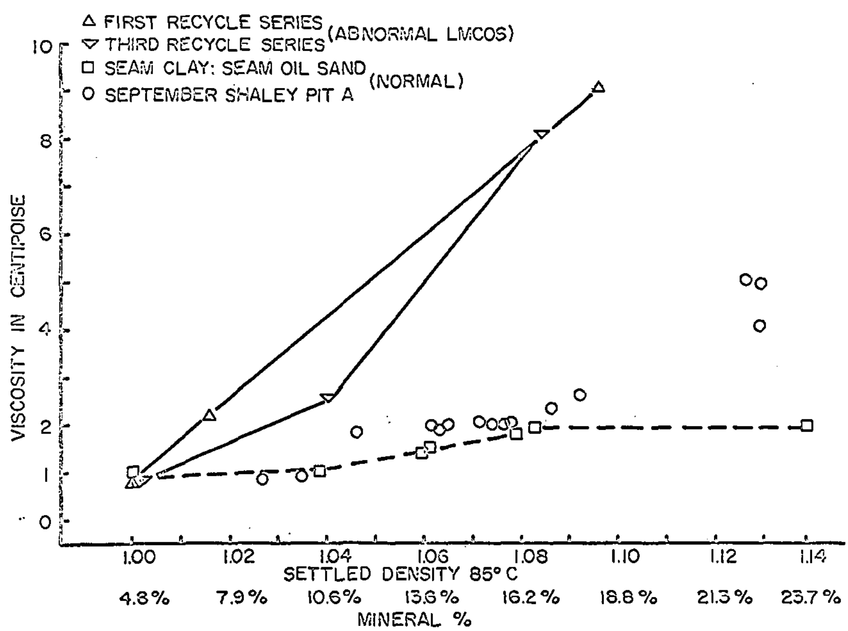

Figure 2. Density-viscosity plot for first lot of Lower Mottled Clay Oil Sand with September Shaley Pit A Oil Sand for comparison.

Laboratory Recycle of Middlings:
High-Fines Oil Sands with Middlings of Abnormal Viscosity

All the laboratory studies were made with a range of different types of oil sands samples so that the general validity of results could be established.

Most of these samples have been from individual seams in the deposit, and we anticipate in general an averaging over a large number of samples. In this section will be described some samples of less common occurrence but of such extreme difference that the properties will be described in some detail.

EXPERIMENTAL

The experimental methods are essentially as in the preceding section. One additional set of data was obtained. The supernatent liquid after centrifuging all the mineral from selected middlings samples was analyzed for certain cations. Sodium, potassium, and calcium concentrations were measured by flame photometry; magnesium was determined by an EDTA titration. The cations held in the exchange capacities of various fine mineral fractions were determined by adding:

1. barium chloride to 0.05 N concentration, or
2. lithium chloride to 0.5 N and analyzing the supernatent liquid as above.

These abnormal oil sand samples were collected from a fresh face near the bottom of the escarpment on Lease 4, 25 miles down river from Fort McMurray. They appeared like a seam of clay with lumps of very rich oil sand interspersed giving a mottled appearance. There were two seams, each 8-12 in. thick, separated by about 6 ft. of rich oil sand. We were in need of high-fines samples and, therefore, chose them among others. These two samples by themselves gave essentially no froth yield although the oil content was at least 10 percent. They were mixed 1:1 with rich oil sand in order to apply the conventional procedures to test them.

RESULTS

Processing Characteristics and Middlings Viscosity of the Lower Mottled Clay Oil Sand (abnormal)

The first abnormal behavior of this oil sand was evidenced in the low froth yield by itself, as mentioned, and then even when mixed 1:1 with a very good oil sand. The results of a recycle series are shown in Table 5. A duplicate run gave essentially the same results.

An example of the extreme difference in rheological properties of this sample is shown in Figure 2. Here it will be noted that after the second recycle the immediate viscosity of the settled middlings is extremely high and as Table 5 shows, separation is not operating. The rheopectic viscosity is even more strikingly different from the immediate viscosity. In the second recycle, the viscosity reached 12-15 centipoise after 15 min. viscometer rotation at 6 r.p.m. In both types of viscosity measurement, there is a significant difference between what we have come to regard as normal behavior and the last sample we have described. For example, for a minimum operable viscosity, the allowable mineral content may be only one-half to one-third that for a sample such as Shaley Pit A. The results for this abnormal Lower Mottled Clay Oil Sand sample have been duplicated with the other seam, the Upper Mottled Clay Oil Sand.

Analysis for Cations in Middlings

The increase in conductance of the middlings during a recycle series parallels the increase in undesirable rheological characteristics. Classic studies in clay chemistry has demonstrated this effect -- flocculation by electrolytes leads to higher viscosities and non-Newtonian rheology. The effect was demonstrated in several middlings samples by removing the ionic impurities; anomalously high viscosities were no longer present in the dialyzed suspension. These data led to measurement of concentrations in the aqueous phase for selected cations, sodium, potassium, magnesium, and calcium. The pH at which the separation is carried out and the nature of the changes with time which we observed led us to eliminate other ions from consideration.

The results of analysis of middlings and the investigation of the exchange cations in the clays are shown in Table 6. The results of immediate interest are in comparing the "no recycle" samples, which are the middlings produced in the first run of a series. The Shaley Pit A shows no divalent cation whereas the Mottled Clay sample is already at 9.6 millinormal concentration. Also, this sample contains a large quantity of magnesium ion in the exchange reservoir of the clay.

Several comments are in order on these results. First, these results at the p.p.m. level

TABLE 4

SUMMARY OF SETTLING RESULTS (DENSITY DECREASE) FROM RECYCLE RUNS ON SEPTEMBER SHALEY PIT A

Time before Decantation	0.58 min. Second Sequence		2 min. Third Sequence		15 min. First Sequence	
Cycle Number	% Mineral*	D_5-C_{15}	% Mineral*	D_5-D_{15}	% Mineral	D_5-D_{15}
1	7.1	0.0019	5.6	0.0009	5.2	0.0010
2	11.7	0.0060	12.0	0.0113	7.9	0.0099
3	17.2	0.0124	14.9	0.0180	9.7	0.0108
4	22.7	0.0235	16.6	0.0139	13.2	0.0099
5	23.9	0.0215	20.7	0.0160	12.8	0.0066
6	34.4	0.0373	21.8	0.0175	15.1	0.0177
7	Inoperable		31.4	0.0167	17.6	0.0228
8			Inoperable		17.7	0.0144
9					18.7	0.0177
10					17.2	0.0162
					Drag rate decreased**	
11					16.8	0.0114
12					15.4	0.0107
13					18.3	0.0118
14					23.1	0.0235
15					21.4	0.0181
16					21.2	0.0177
17					21.8	0.0169
Average-over		0.0237 last four		0.0164 last five		0.0157 last seven

* Mineral content determined from Decanted Middlings Density.

** Absolute drag rate usual 60 out of 260 ml in all except following Cycle 11 in First Sequence. Final absolute drag rate, 35 out of 260 ml.

TABLE 5

MIDDLINGS RECYCLE SERIES ON 1:1 LOWER MOTTLED CLAY OIL SAND - GOOD OIL SAND

Conditions: 3" Stirred Reactor, 50 RPM, 15 min. middlings decant
Mottled Oil Sand, 9.9% Oil; good oil sand, 13.5% oil

Cycle No.	#/Ton NaOH	Middlings pH	% Bitumen	% Recovered Bitumen in: Froth	Midd	Tails	% Min. in Froth Min(DB)	Analysis of Middlings % Min	% Oil	Conductance of Decanted Middlings
1	0.875	8.35	36.5	40.8	58.3	0.9	7.6	12.2	4.8	1000
2	1.0	8.3	29.6	21.8	65.6	12.6	11.6	16.4	9.8	1675
3	1.0	8.5	13.0	7.9	79.5	12.6	27.5	16.8	12.8	1975
4	0.875	8.4	28.2	10.2	85.7	4.1	26.6	22.5	15.6	1320

TABLE 6

DETERMINATION OF THE CATION EXCHANGE CAPACITY AND INDIVIDUAL EXCHANGE CATIONS OF CLAY IN LABORATORY MIDDLINGS

Sample	Displacing Reagent*	Total conc. of cations, mN Na	K	Mg	Ca	C.E.C. meq./100 g.
September Shaley Pit A						
No recycle	$BaCl_2$	5.8	ND	1.2	4.2	10.5
No recycle	LiCl	4.6	ND	1.0	4.7	11.5
No recycle	None	3.1	ND	ND	ND	
Fine Mineral after settling						
7th recycle	$BaCl_2$	16.9	ND	1.6	8.9	21.0
7th recycle	LiCl	14.1	ND	1.7	10.1	19.0
7th recycle	None	8.2	ND	3.9	ND	
Lower Mottled Clay Oil Sands						
No recycle	$BaCl_2$	14.5	ND	11.4	9.3	12.0
No recycle	LiCl	6.8	ND	15.8	6.4	12.0
No recycle	None	5.7	ND	9.6	ND	

*Reagent used to displace exchange cations from clay in sample. $BaCl_2$, 0.05N; LiCl, 0.5N in sample. 85 °C

"None," the control, shows the amounts of cations in the aqueous phase before addition of the displacing reagent.

ND = not detected; lower limit is probably 5 ppm or less.

TABLE 7

EXPERIMENTS ON THE INTERACTION OF ADDED ELECTROLYTES AND MINERAL FINES IN THE HOT WATER EXTRACTION PROCESS

All runs at operating pH, 8.4; no recycle

Percent Added Clay	Added Mg^{++} mN	Primary Froth Yield %	% Mineral in Froth, D.B.
Mixture of high quality oil sand* with added clay			
0	0	83	0.8
30	0	63	5.7
0	2	82	6.5
30	2	5	11.1
0	6	73	9.0
10	0	91	5.1
10	6	57	2.5
September Shaley Pit A			
0	0	58	9.0
0	2	23	9.6

*This oil sand was chosen as the base because it has as close to zero fines content as we have available; 15.5% oil; less than 2% fines.

are subject to a random error, and this is evidenced by a rather large difference of the sets of sodium analysis. However, when the results of 4-5 analyses are combined additively, quite good agreement is obtained on the Cation Exchange Capacity (C.E.C.). Second, the samples with "no recycle" represent middlings as generated in the laboratory with no settling. Hence higher percentages of non-clay minerals will result in a lower C.E.C. The "7th recycle" sample represents fine mineral after settling and hence has a higher percentage clay, smaller particles, and probably a somewhat higher percentage of high exchange clays such as montmorillonite. These measurements of C.E.C. are in good agreement with the values which can be calculated from the known mineralogical composition.

Effect of Cation Concentrations on Middlings Viscosity

As an example of the effect of cations on the viscosity of clay suspensions, measurements were made on a sample of settled middlings which was normal rheology. To this sample (about 9 percent fine mineral) was added known quantities of two cations. These added cations were beyond the cations already present in the middlings from the normal procedure. The results are as follows:

	Viscosity, centipoise	
Added Cation	Immediate	Rheopectic, after 15 min., 6 r.p.m.
None	3	5
6.6 mN Na^+	5	75
0.7 mN Ca^{++}	5	50

These results show the effect of divalent cations as much greater than the monovalent ions, in agreement with the generalizations such as the Hofmeister series. These measurements were made to confirm that the response of the middlings clay suspensions to cations fell in the usual pattern.

Controlled Experiments on the Effect of Cations on the Extraction Process

The effect of added ions on the hot water extraction process was first reported by Clark and Pasternak (3); the Clark procedure was adopted for the Edna, California, oil sands by using a cold water wash to remove soluble salts (4). Clark's work was prompted by difficulties in processing a deposit just up the Clearwater River from Fort McMurray. Although no evidence was given, he believed them to be soluble salts present in the formation. He then showed that rather massive (by our results) doses of magnesium or calcium salts could reduce froth yields. In the experiments to test the effect of cations, Clark used oil sands of as low fines content as could be found. We agree that M^{++} concentrations of the order of 20-60 millinormal in the middlings are required to decrease froth yield for low-fines oil sands.

Three factors prompted us to design the experiment to be described.

1. Although there is a rough inverse correlation between oil content and primary froth yield, the spread of the points is very wide. For example, different oil sands of 10 percent oil content have been found that yield primary froth in the range from zero to 90 percent. An additional parameter has long been sought.
2. The behavior of medium and poor grade oil sands in processing and the properties of middlings when electrolytes have been added suggest that cations have an effect in the primary separation process as well as through increasing the viscosity for the settling step.
3. The phenomenon described in (2) is frequently associated with the mineral content of the separated oil. This mineral content is vital in determining the proportion of the oil which will float as froth. There is reason to believe that in the presence of cations, the separation of the mineral becomes less and less effective.

EXPERIMENTAL

A series of controlled experiments were organized in which the separate effects of cations and clay were evaluated and then the interaction evaluated in a further experiment. The standard procedure of conditioning and flooding was used; the additives were introduced in the first stage of conditioning. As a base for the experiments an oil sand as free from mineral fines as possible was used. Clay from a uniform seam of essentially zero oil content was used. The complete control was not possible in the experiment on Shaley Pit A (17 percent fines), but it was used because it represents the only other important type of high-fines oil sand. Magnesium chloride was used to supply the cation because the analytical results had indicated that cation. Earlier results indicated that the Shaley Pit A had no magnesium in the initial middlings, and the seam clay yielded 2.0 mN magnesium.

RESULTS

The results of these experiments are shown in Table 7. For both of the basic types of high-fines oil sand the conclusion is unequivocal: the combination of mineral fines and a cation such as magnesium results in drastically lowered primary froth yields. The mineral content of the froth is of limited value because it is based only on the fraction of the oil that floats, and that fraction is, of course, only the portion of low mineral content. For a given sample and procedure, flotation gas content is reasonably uniform. To return to the main point, there is now clear-cut experimental evidence for an additional parameter to help us understand differences in primary froth yield. This parameter, liberation of soluble cations, is primarily effective in its interaction with mineral fines (clay).

DISCUSSION

In describing the development of the understanding of the oil sand processing in this paper, many of the points have already been discussed. In reviewing the series of experiments the following points are worthy of emphasis in summary.

1. In laboratory work with the stirred reactor, a progressively decreasing solids content yields a froth of minimum, uniform mineral content. One of the key elements seems to be high shear in a relatively viscous mixture. Conditioning with fresh water produces a better yield and quality of froth than when recycle middlings are used in conditioning.
2. The laboratory middlings recycle procedure provides an excellent tool for studying the properties of middlings. A plot of middlings viscosity against mineral content is a useful method of characterizing the settling operability of a given oil sand.
3. As inoperability is approached, the viscosity plot begins to curve upward sharply. The behavior can be understood from a simple mathematical expression of the kinetic factors involved:

   Viscosity increase (or degree of agglomeration) = constant X (mineral fines)^2

   X (soluble electrolytes)

   This expression shows that the components which accumulate during recycle jointly will produce a third order effect in the kinetics of clay agglomeration. This agglomeration results in sharp upward rise in viscosity at high levels of mineral content.
4. All comparisons we have been able to make to performance of the Field Test Unit show complete correspondence to laboratory results such as in Item 3 above. For example, electron micrographs of mineral fines show essentially the same morphology of the very fine mineral in samples from both sources.
5. The contribution of soluble electrolytes to undesirable rheological properties of middlings has been assessed in a number of ways.
   a. The increase in conductivity of the middlings in successive cycles is a good indicator of this factor. The results are in accord with the several accepted reactions of sodium hydroxide with clay.
   b. Dialysis to remove electrolytes eliminates the undesirable non-Newtonian rheology.
   c. As expected, divalent cations have 5 to 10 times the effect for monovalent cations at equivalent concentrations.
   d. Analysis of the supernatent water shows the presence of Mg^{++} in samples which have non-Newtonian rheology. These samples were "normal" oil sands after 7 recycles or "abnormal" samples in the first cycle.
   e. Determination of the exchange cations in the fine mineral of these samples shows that the abnormal samples contain large amounts of Mg^{++}.

   This and other evidence leads us to believe that these ions originate in both the exchange capacity of the clay and in the connate water.
6. If appreciable amounts of the "abnormal" type of oil sands are encountered in large

scale processing, the middlings density will have to be held at levels much lower than normal. A control on make-up water from middlings viscosity would be desirable.

7. Results of the preceeding studies suggested that soluble electrolytes could be an important parameter in the froth yield from oil sands of medium and high fines content. A set of controlled experiments showed that low levels of added electrolytes had no effect on oil sand free of fines. When clay was present, interaction of the clay and the electrolyte led to pronounced decreases in froth yield. Therefore, the primary froth yield of a given average of worse oil sand will be determined by the fines content plus the amount of (divalent) cation released to the process water.

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